

PATENT SPECIFICATION

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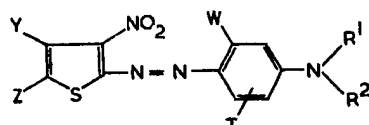


(54) DISPERSE AZO DYESTUFFS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to disperse monoazo dyestuffs which are valuable for colouring synthetic textile materials.

15 According to the invention there are provided the water-insoluble monoazo dyestuffs, free from sulphonic acid and carboxylic acid groups, which are of the formula:—



20 wherein Y is hydrogen, lower alkyl, optionally substituted phenyl or nitro; Z is nitro, cyano, optionally substituted phenyl, optionally substituted lower alkoxy carbonyl or carbonamido; T is hydrogen, optionally substituted lower alkyl or optionally substituted lower alkoxy; W is an acylamino group of the formula:—



wherein X¹ is hydrogen or lower alkyl, X² is hydrogen or an optionally substituted hydrocarbon or heterocyclic radical, and A is a direct link or —O— or

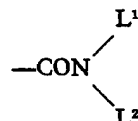


and R¹ and R² each independently represent a hydrogen atom, alkyl or alkyl substituted by a substituent which does not contain a carbocyclic ring system directly attached to a carbon atom of the alkyl chain, or R¹ and R² together form with the nitrogen atom N a 5- or 6-membered nitrogen-containing heterocyclic ring.

Throughout this specification the terms “lower alkyl” and “lower alkoxy” are used to denote alkyl and alkoxy radicals respectively containing from 1 to 4 carbon atoms.

As examples of the lower alkyl radicals represented by Y and X¹ there may be mentioned methyl, ethyl, *n*-propyl and *n*-butyl.

As examples of the substituted phenyl radicals represented by Y and Z there may be mentioned tolyl, chlorophenyl, nitrophenyl and nitrotolyl. As examples of the optionally substituted lower alkoxy carbonyl radicals represented by Z there may be mentioned methoxy carbonyl and ethoxycarbonyl, hydroxy lower alkoxy carbonyl such as β -hydroxyethyloxy-carbonyl, cyano lower alkyl such as β -cyano-ethoxycarbonyl, and lower alkoxy lower alkoxy carbonyl such as β -methoxyethoxycarbonyl. The carbonamido groups represented by Z are of the formula

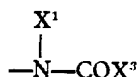


wherein L¹ is hydrogen, lower alkyl or phenyl and L² is hydrogen or lower alkyl; and as examples of the said groups there may be mentioned carbonamido itself and N-methyl and N:N-diethylcarbonamido.

As examples of the optionally substituted lower alkyl radicals represented by T there may be mentioned methyl, ethyl, *n*-propyl and *n*-butyl, hydroxy lower alkyl such as β -

hydroxyethyl, lower alkoxy lower alkyl such as methoxymethyl, and lower alkoxy-carbonyl lower alkyl such as ethoxycarbonylmethyl. As examples of the optionally substituted lower alkoxy radicals represented by T there may be mentioned methoxy and ethoxy, hydroxy lower alkoxy such as β -hydroxyethoxy, lower alkyl-carbonyloxy lower alkoxy such as β -acetoxy-ethoxy, lower alkoxy lower alkoxy such as β -methoxyethoxy and lower alkoxy-carbonyl lower alkoxy such as β -methoxycarbonyl ethoxy. It is preferred that T is attached to the benzene ring in para position to W, and that T represents hydrogen, lower alkyl or lower alkoxy.

As examples of the radicals represented X² there may be mentioned alkyl in particular lower alkyl such as methyl, ethyl, propyl and butyl, hydroxy lower alkyl such as β -hydroxyethyl, cyano lower alkyl such as β -cyanoethyl, chloro lower alkyl such as chloromethyl, lower alkoxy-carbonyl lower alkyl such as acetylmethyl, lower alkyl carbonyloxy lower alkyl such as β -acetoxyethyl, phenyl and substituted derivatives thereof such as tolyl, anisyl, dimethoxyphenyl and chlorophenyl, and heterocyclic radicals such as pyrid-2-yl and thien-2-yl radicals. It is however preferred that W represents an acylamino group of the formula

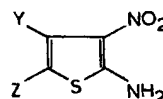


wherein X¹ and X² are each independently hydrogen or lower alkyl, and preferably X¹ is hydrogen.

The alkyl radicals represented by R¹ and R² are preferably lower alkyl radicals such as methyl, ethyl, *n*-propyl and *n*-butyl radicals. The substituted alkyl radicals represented by R¹ and R² are preferably substituted lower alkyl radicals, for example hydroxy lower alkyl such as β -hydroxyethyl, δ -hydroxybutyl and β , γ -dihydroxypropyl, lower alkoxy lower alkyl such as β -ethoxyethyl and γ -methoxypropyl, cyano lower alkyl such as β -cyanoethyl, chloro lower alkyl such as β -chloroethyl and γ -chloropropyl, lower alkylcarbonyloxy lower alkyl such as β -acetoxyethyl, lower alkoxy-carbonyl lower alkyl such as β -(methoxy- or ethoxy-carbonyl) ethyl and α , β -di(methoxy-carbonyl)ethyl, hydroxy lower alkoxy carbonyl lower alkyl such as β -(β' -hydroxyethoxy-carbonyl)ethyl, lower alkoxy lower alkoxy-carbonyl lower alkyl such as β -(β' -methoxyethoxycarbonyl)ethyl, lower alkoxy lower alkoxy lower alkoxy-carbonyl lower alkyl such as β -[β' -(β'' -methoxyethoxy)ethoxy-carbonyl]ethyl, phenylcarbonyloxy lower alkyl such as β -benzoyloxy ethyl, lower alkoxy-carbonyloxy lower alkyl such as β -ethoxycarbonyloxy ethyl, lower alkylsulphonyloxy lower alkyl such as β -methoxysulphonyloxyethyl, lower alkylcarbonyl lower alkyl such as β -acetyloxyethyl, lower alkoxy lower alkyl carbon-

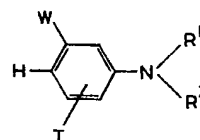
yl lower alkyl such as β -(β' -methoxypropionyl)ethyl, benzoyl lower alkyl such as benzoylmethyl, lower alkoxy-carbonyl lower alkoxy lower alkyl such as β -(β' -methoxycarbonylethoxy)ethyl, lower alkoxy carbonyl lower alkylthio lower alkyl such as β -(ethoxycarbonylmethylthio)ethyl, cyclohexyloxy-carbonyl lower alkyl such as β -cyclohexyloxy-carbonylethyl, lower alkyl sulphonyl lower alkyl such as β -methylsulphonyl ethyl, and phenoxycarbonyloxy lower alkyl such as β -phenoxycarbonyloxyethyl and β -anisylcarbonyloxyethyl. As examples of the 5- or 6-membered nitrogen-containing heterocyclic rings formed by R¹, R² and the nitrogen atom N there may be mentioned pyrrolidone, morpholine and piperidine rings.

According to a further feature of the invention there is provided a process for the manufacture of the azo dyestuffs as hereinbefore defined which comprises diazotising an amine of the formula:—



Formula I

and coupling the resulting diazo compound with a coupling component of the formula:—



wherein Y, Z, W, T, R¹ and R² have the meanings stated, the amine and coupling component being free from carboxylic acid and sulphonic acid groups.

The process of the invention can be conveniently carried out by adding sodium nitrite to a solution or dispersion of the amine in a strong inorganic acid or an aqueous solution thereof, or preferably by stirring the amine with nitrosylsulphuric acid, and adding the resulting solution or dispersion of the diazo component to a solution of the coupling component in water or in a mixture of water and a water-miscible organic liquid, if necessary adjusting the pH of the mixture to facilitate the coupling reaction, and finally isolating the resulting dyestuff by conventional methods.

The amines of Formula I can themselves be obtained by the conventional methods used for the production of thiophene derivatives. Thus, for example, a 2-halogenothiophene can be nitrated and the halogen atom in the 2-position is then converted to an amino group by treatment with ammonia. Alternatively 2-aminothiophenes containing electron withdrawing

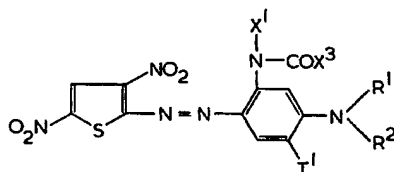
groups can be prepared by conventional methods from compounds obtained by the methods described in *Chemische Berichte*, Volume 98 at page 3571 (1965) and Volume 99 at page 94 (1966).

As specific examples of amines of Formula I there may be mentioned, for example, 2-amino - 3:5 - dinitrothiophene, 2 - amino - 3:4:5 - trinitrothiophene, and 2 - amino - 3-nitro - 5 - (carbonamido, cyano or methoxy carbonyl) thiophene. The preferred amine is 2 - amino - 3:5 - dinitrothiophene.

As specific examples of the said coupling components there may be mentioned N:N - diethyl - *m* - aminoacetanilide, N:N - di(β -acetoxyethyl) - *m* - aminoacetanilide, 2 - methoxy - 5 - (formylamino- or acetylamino) - N - [β - (methoxyethoxycarbonyl)ethyl] - aniline, *m* - N:N - diethylamino - β - chloropropionanilide and *m* - N:N - di - *n* - butylformanilide.

A preferred class of the dyestuffs of the invention comprises the dyestuffs wherein Y is hydrogen and Z is nitro.

A second preferred class of the dyestuffs of the invention comprises the dyestuffs of the formula:—



wherein R¹, R², T¹, X¹ and X³ have the meanings stated.

The azo dyestuffs of the invention are valuable for colouring synthetic textile materials in particular secondary cellulose acetate and cellulose triacetate textile materials, polyamide textile materials such as polyhexamethylene adipamide textile materials, and, above all, aromatic polyester textile materials such as polyethylene terephthalate textile materials. Such materials can be in the form of filaments, fibres or woven or knitted materials.

The said azo dyestuffs can be applied to the synthetic textile materials by methods which are conventionally employed in applying disperse dyestuffs to such textile materials. Thus the dyestuffs in the form of aqueous dispersions can be applied by dyeing, padding or printing processes using the conditions and other additives which are conveniently used in carrying out such processes. Alternatively the said dyestuffs can be applied to synthetic textile materials by solvent methods of dyeing, for example by applying a solution or dispersion of the dyestuff in perchloroethylene optionally containing a minor amount of water to the textile material preferably at elevated tempera-

ture. The dyestuffs may also be used to colour synthetic polymers by melt colouration, for example using late injection techniques, followed by melt spinning of the coloured polymers into fibres or filaments. Alternatively the dyestuffs can be applied to synthetic textile materials by the process of transfer colour printing.

When applied to synthetic textile materials the azo dyestuffs of the invention give violet to green colourations which have excellent fastness to light and to wet and to dry heat treatments both before and after heat setting. The said dyestuffs also have high tinctorial strength, exhaust well and have excellent dyeing, leveling, temperature range and build up properties on synthetic textile materials, particularly aromatic polyester textile materials, thus enabling heavy depths of shade to be readily obtained.

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight.

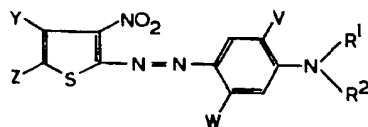
Example 1.

7.6 Parts of sodium nitrite are added to 90 parts of sulphuric acid, the temperature being allowed to rise to 30°C. The mixture is then cooled to 5°C and a mixture of 50 parts of propionic acid and 300 parts of acetic acid added, the temperature of the mixture being allowed to rise to 15°C and then maintained at this temperature. The mixture is then cooled to 0°C, 18.9 parts of 2 - amino - 3:5-dinitrothiophene are added over 30 minutes and the mixture is stirred for 20 minutes at 0°C. The resulting solution is added to a solution of 31 parts of 2 - methoxy - 5 - acetyl-amino - N - β - [β - (methoxyethoxycarbonyl)ethyl]aniline in 300 parts of water containing 30 parts of a concentrated aqueous solution of hydrochloric acid and 350 parts of ice. The mixture is stirred for 50 minutes at 0°C and the precipitated dyestuff is then filtered off, washed with water and dried.

When applied to aromatic polyester textile materials from an aqueous dispersion the dyestuff yields green shades of excellent fastness properties.

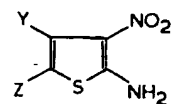
The 2 - amino - 3:5 - dinitrothiophene was itself obtained by reacting the sodium salt of cyanoacetic acid with the dimer of mercaptoacetaldehyde in aqueous medium at 80°C, cooling to 20°C, adding acetic anhydride whilst maintaining the pH at 6—7, acidifying and isolating the 2 - acetylaminothiophene - 3-carboxylic acid. This was then dinitrated in sulphuric acid medium at 0°C, the resulting 2 - acetyl-amino - 3:5 - dinitrothiophene being isolated and then deacetylated by heating in an aqueous solution of sulphuric acid.

Table I gives further Examples of the dyestuffs of the invention of the formula



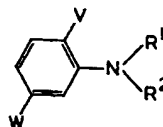
5 the symbols of which have the values given in the respective columns of the Table, whilst the last column of the Table gives the shades obtained when the dyestuffs are applied to an aromatic polyester textile material.

The dyestuffs of these Examples were obtained by diazotising the appropriate amine of the formula:—



10

and coupling the resulting diazo compound with the appropriate coupling component of the formula



using methods similar to that described in 15 Example 1.

TABLE I

Example	Y	Z	V	W	R ¹	R ²	Shade
2	H	nitro	H	acetyl amino	ethyl	ethyl	Bluish-green
3	methyl	"	"	"	β -acetoxyethyl	β -acetoxyethyl	"
4	nitro	"	methoxy	"	H	β -(β' -methoxyethoxy-carbonyl)ethyl	Green
5	H	methoxy carbonyl	H	"	ethyl	ethyl	Greenish-blue
6	"	N:N-diethyl-carbonamido	"	"	"	"	"
7	"	cyano	"	"	"	"	"
8	"	nitro	methoxy	"	"	"	Green
9	"	"	"	"	H	β -methoxyethyl	"
10	"	"	H	"	β -(β' -methoxy-ethoxycarbonyl)ethyl	β -(β' -methoxyethoxy-carbonyl)ethyl	Greenish-blue
11	"	"	"	"	H	"	"
12	"	"	"	"	β -methoxyethyl	β -methoxyethyl	Bluish-green
13	"	"	methoxy	"	β -(β' -methoxy-ethoxycarbonyl)ethyl	ethyl	Green

TABLE I (Continued)

Example	Y	Z	V	W	R ¹	R ²	Shade
14	H	nitro	H	chloroacetyl- amino	ethyl	ethyl	Bluish-green
15	"	"	"	acetylamino	β -cyanoethyl	β -(β' -methoxyethoxy- carbonyl)ethyl	Greenish-blue
16	H	"	"	"	"	H	"
17	"	"	"	"	β -hydroxyethyl	β -hydroxyethyl	Bluish-green
18	"	"	"	"	β -acetoxyethyl	β -acetoxyethyl	Greenish-blue
19	"	"	"	"	β -chloroacetoxyethyl	β -chloroacetoxyethyl	"
20	"	"	"	"	β -hydroxypropyl	β -hydroxypropyl	Bluish-green
21	"	"	"	"	β -acetoxypropyl	β -acetoxypropyl	Greenish-blue
22	"	"	"	α -acetylacetyl- amino	H	H	"
23	"	"	"	phenoxy- carbonylamino	β -acetoxyethyl	β -acetoxyethyl	"
24	"	"	"	formylamino	n-butyl	n-butyl	Bluish-green
25	"	"	"	"	β -benzoyloxyethyl	β -benzoyloxyethyl	Greenish-blue
26	"	"	methoxy	3:4-dimethoxy- benzoylamino	β -methoxycarbonyl- ethyl	β -methoxycarbonyl ethyl	Green
27	"	"	ethoxy	acetylamino	β -ethoxycarbonyl- oxyethyl	β -ethoxycarbonyloxy- ethyl	"

TABLE I (Continued)

Example	Y	Z	V	W	R ¹	R ²	Shade
28	H	nitro	H	acetylamino	γ -hydroxypropyl	γ -hydroxypropyl	Bluish-green
29	"	"	"	"	ethyl	n-dodecyl	"
30	"	"	"	"	ethyl	ω -hydroxypentyl	"
31	"	"	methoxy	N-methylacetyl- amino	β -acetoxyethyl	β -acetoxyethyl	Green
32	"	"	"	formylamino	β -(cyanoacetoxy) ethyl	β -cyanoacetoxyethyl	"
33	"	"	"	β -acetoxypropionylamino	β -acetoxyethyl	β -acetoxyethyl	"
34	"	"	"	methoxycarbonyl- amino	β -(allyloxycarbonyl)- ethyl	β -(allyloxycarbonyl) ethyl	"
35	"	"	H	acetylamino	β -methylsulphonyl oxyethyl	β -methylsulphonyloxy- ethyl	Greenish-blue
36	"	"	"	"	ethyl	β -succinimidoethyl	Bluish-green
37	"	"	"	ureido	H	H	Greenish-blue
38	"	"	methoxy	"	β -acetoxyethyl	β -acetoxyethyl	Green
39	"	"	"	"	β -acetyllethyl	β -acetyllethyl	"
40	"	"	"	acetylamino	H	H	Greenish-blue
41	"	"	"	"	methyl	β -cyanoethyl	"

TABLE I (Continued)

Example	Y	Z	V	W	R ¹	R ²	Shade
42	H	nitro	methoxy	thien-2-yl carbonylamino	ethyl	ethyl	Bluish-green
43	H	"	"	ethylureido	β -acetoxyethyl	β -acetoxyethyl	"
44	"	"	H	N:N-diethyl- ureido	β -acetoxyethyl	β -acetoxyethyl	"
45	"	"	"	β -hydroxypro- pionylamino	ethyl	ethyl	"
46	"	"	"	"	β -chloroethyl	β -chloroethyl	Greenish-blue
47	"	"	"	acetylamino	β -(β' -methoxy- propionyl)ethyl	ethyl	Bluish-green
48	"	"	"	"	β : γ -dihydroxypropyl	"	"
49	"	"	"	"	α : β -di(ethoxycarbonyl) ethyl	"	"
50	"	"	"	"	β -(β' -cyanoethoxy)ethyl	"	"
51	"	"	"	"	methyl	β -(β' -methoxycarbonyl- ethoxy)ethyl	"
52	"	"	"	"	ethyl	β -(ethoxycarbonylmethyl- thio)ethyl	"
53	"	"	ethoxy carbonyl- methyl	"	"	ethyl	"
54	"	"	methyl	"	H	β -hydroxyethyl	Green

TABLE I (Continued)

Example	Y	Z	V	W	R ¹	R ²	Shade
55	H	nitro	β -acetoxy-ethoxy	acetyl amino	β -acetoxyethyl	β -acetoxyethyl	Bluish-green
56	"	"	H	"	β -(cyclohexylcarbonyl-oxy)ethyl	H	Greenish-blue
57	"	"	"	"	ethyl	benzoylmethyl	"
58	"	"	"	"	β -(cyclohexyloxy-carbonyl)ethyl	β -(cyclohexyloxy-carbonyl)ethyl	"
59	"	"	"	"	ethyl	β -(<i>p</i> -anisyl oxy-carbonyloxy)ethyl	Bluish-green
60	"	"	"	"	ethyl	β -(diethylamino-carbonyloxy)ethyl	"
61	"	"	"	"	"	β -(<i>m</i> -toluidino-carbonyl)ethyl	"
62	"	"	"	"	"	β -(ethylsulphonyl)ethyl	Greenish-blue
63	"	"	"	"	"	β -(bromoacetyl amino)-ethyl	Bluish-green
64	methyl	"	"	"	β -hydroxyethyl	β -hydroxyethyl	Greenish-blue
65	"	"	"	"	ethyl	ethyl	"
66	"	"	methoxy	"	n-butyl	β -(β' -methoxyethoxy-carbonyl)ethyl	"

TABLE I (Continued)

Example	Y	Z	V	W	R ¹	R ²	Shade
67	methyl	nitro	H	acetyl amino	β -cyanoethyl	β -(β' -methoxyethoxy carbonyl)ethyl	Blue
68	H	"	methoxy	"	H	β -[β' -(β'' -methoxyethoxy)ethoxy]carbonyl ethyl	Green
69	"	methoxy carbonyl	"	"	"	β -(β' -methoxyethoxy carbonyl)ethyl	Blue
70	"	ethoxy carbonyl	H	"	β -methoxy carbonyl ethyl	β -methoxy carbonyl ethyl	"
71	"	β -methoxyethoxy carbonyl	"	"	ethyl	ethyl	"
72	"	nitro	"	"	β -(β' -ethoxy carbonyl-propionyloxy)ethyl	β -(β' -ethoxy carbonyl-propionyloxy)ethyl	Greenish-blue
73	"	carbonamido	"	"	β -acetoxylethyl	β -acetoxylethyl	Blue
74	"	N-phenyl carbonamido	"	"	β -hydroxyethyl	β -hydroxyethyl	"
75	"	cyano	"	"	β -acetoxylethyl	β -acetoxylethyl	Greenish-blue
76	"	"	methoxy	"	H	β -(β' -methoxyethoxy carbonyl)ethyl	Bluish-green

TABLE I (Continued)

Example	Y	Z	V	W	R ¹	R ²	Shade
77	H	cyano	ethoxy	acetyl amino	ethyl	β -(β' -methoxyethoxy-carbonyl)ethyl	Bluish-green
78	"	"	H	ethoxycarbonyl-amino	β -acetoxyethyl	β -acetoxyethyl	Greenish-blue
79	"	"	"	acetyl amino	β -cyanoethyl	β -(β' -methoxyethoxy-carbonyl)ethyl	"
80	"	"	"	"	H	ethyl	"
81	methyl	"	"	"	ethyl	"	"
82	p-nitro-phenyl	nitro	"	"	β -hydroxyethyl	β -hydroxyethyl	Green
83	H	2-nitro-4-methyl-phenyl	"	"	ethyl	ethyl	Blue
84	"	cyano	"	"	β -hydroxyethyl	β -hydroxyethyl	"
85	"	"	"	"	β -methoxyethyl	β -methoxyethyl	Greenish-blue
86	"	"	"	"	β -acetyl ethyl	ethyl	"
87	"	"	"	"	β -propionyloxyethyl	β -propionyloxyethyl	"
88	"	"	"	ureido	ethyl	ethyl	"
89	"	"	"	benzoyl amino	β -hydroxyethyl	β -hydroxyethyl	"

Table II gives further Examples of the dyestuffs of the invention which are obtained by diazotising 2 - amino - 3:5 - dinitrothiophene and coupling the resulting diazo compound with the coupling components listed in

the second column of the table using methods similar to that described in Example 1. The shades obtained on aromatic polyester textile materials from the resulting dyestuffs are given in the last column of the table.

TABLE II

Example	Coupling Component	Shade
90	N-(3-acetylaminophenyl)pyrrolidine	Bluish-green
91	N-(3-acetylaminophenyl)morpholine	„ „
92	2-methyl-3-acetylaminobenzene	„ „

The 2 - amino - 3:5 - dinitro - 4 - methylthiophene used in the above examples was itself obtained as follows:—

15 Chloroacetone was reacted with sodium hydrosulphide in aqueous medium, and the resulting solution was treated with ethylcyanoacetate in the presence of triethylamine at the boil. Addition of water precipitated 2-amino - 3 - ethoxycarbonyl - 4 - methylthiophene which was acetylated and then heated with an aqueous solution of sodium hydroxide to give 2 - acetylmino - 4 - methylthiophene-3 - carboxylic acid. This was decarboxylated by heating in N:N - diethylaniline at 220°C, the product dinitrated in sulphuric acid medium at -5°C, and then deacetylated by heating in an aqueous solution of sulphuric acid.

20 The 2 - amino - 3:4:5 - trinitrothiophene was obtained by reacting 2 - bromo - 3:4:5-trinitrothiophene (Journal of Organic Chemistry 1957 at page 1588) with ammonia in tetrahydrofuran.

25 The 2 - amino - 3 - nitro - 5 - (N:N-diethylcarbamoyl)thiophene was obtained by reacting 2 - bromo - 3 - nitrothiophene - 5-carboxylic acid (Chemical Abstracts 1963 at page 3860h) with thionyl chloride in toluene in the presence of dimethylformamide, and subsequently reacting with diethylamine followed by treatment with ammonia to replace the bromine atom by an amino group. The 2-amino - 3 - nitro - 5 - carbamoylthiophene and 2 - amino - 3 - nitro - 5 - (N - phenylcarbamoyl)thiophene were prepared in an analogous manner, the diethylamine being replaced by ammonia and by aniline.

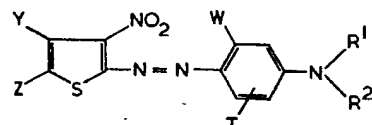
30 The 2 - amino - 3 - nitro - 5 - methoxycarbonylthiophene was prepared by esterifying 2 - bromo - 3 - nitrothiophene - 5 - carboxylic acid using a 9 % solution of sulphuric acid in methanol and subjecting the bromoester to reaction with a concentrated aqueous solution of ammonia in the presence of dimethylformamide. The 2 - amino - 3 - nitro - 5 - ethoxycarbonylthiophene was prepared in an analogous manner. The 2 - amino - 3 - nitro-

5 - (β - methoxyethoxycarbonyl)thiophene was prepared by transesterification of 2 - amino - 3 - nitro - 5 - methoxycarbonylthiophene by heating it in β-methoxy ethanol in the presence of tetrabutyltitanate.

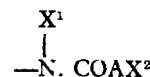
60 The 2 - amino - 3 - nitro - 5 - cyanothiophene was prepared by converting the oxime of 2 - acetylmino - 5 - formylthiophene (Journal of the Chemical Society 1955 at page 1701 to the 5-cyano compound by heating it with acetic anhydride, nitrating in a mixture of acetic acid and acetic anhydride at 40°C, and finally deacetylating the compound.

WHAT WE CLAIM IS:—

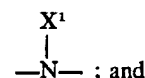
1. The water-insoluble monoazo dyestuffs, free from sulphonic acid and carboxylic acid groups, which are of the formula:—



75 wherein Y is hydrogen, lower alkyl, optionally substituted phenyl or nitro; Z is nitro, cyano, optionally substituted phenyl, optionally substituted lower alkoxy carbonyl or carbonamido; T is hydrogen, optionally substituted lower alkyl or optionally substituted lower alkoxy; W is an acylamino group of the formula:—



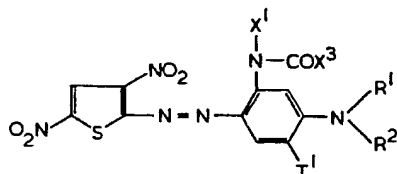
80 wherein X¹ is hydrogen or lower alkyl, X² is hydrogen or an optionally substituted hydrocarbon or heterocyclic radical, and A is a direct link or —O— or



5 R^1 and R^2 each independently represent a hydrogen atom, alkyl or alkyl substituted by a substituent which does not contain a carbocyclic ring system directly attached to a carbon atom of the alkyl chain, or R^1 and R^2 together form with the nitrogen atom N a 5- or 6- membered nitrogen-containing heterocyclic ring.

10 2. The dyestuffs claimed in Claim 1 wherein Y is hydrogen and Z is nitro.

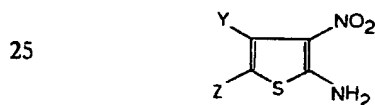
3. The dyestuffs claimed in Claim 1 or Claim 2 which are of the formula:—



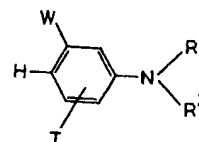
15 wherein R^1 and R^2 have the meanings stated in Claim 1, T^1 is hydrogen, lower alkyl or lower alkoxy, and X^1 and X^3 are each independently hydrogen or lower alkyl.

20 4. The dyestuffs as claimed in any one of Claims 1 to 3 as hereinbefore particularly described especially with reference to any one of the Examples.

5. Process for the manufacture of the dyestuffs as claimed in Claim 1 which comprises diazotising an amine of the formula:—



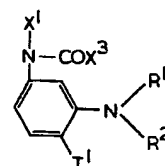
and coupling the diazo compound with a coupling component of the formula:—



wherein Y, Z, T, W, R^1 and R^2 have the meanings stated in Claim 1, the amine and coupling component being free from carboxylic acid and sulphonic acid groups.

6. Process as claimed in Claim 5 wherein the amine is 2-amino-3,5-dinitrothiophene.

7. Process as claimed in Claim 5 or Claim 6 wherein the coupling component is of the formula:—



wherein R^1 and R^2 have the meanings stated in Claim 1, and T^1 , X^1 and X^3 the meanings stated in Claim 3.

8. Process for the manufacture of the dyestuffs as claimed in any one of Claims 1 to 4 as hereinbefore particularly described especially with reference to any one of the Examples.

9. Process for colouring synthetic textile materials which comprises applying to the textile material a dyestuff as claimed in any one of Claims 1 to 4.

10. Process as claimed in Claim 9 wherein the textile material is an aromatic polyester textile material.

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